

MEMOIRS
OF THE
COLLEGE OF SCIENCE

KYOTO IMPERIAL UNIVERSITY

SERIES A

VOL. VII, No. 3

MARCH 1924

KYOTO

Über die Zementierung Kleiner Eisenstücke

von

Denzo Uno.

(Eingegangen bei der Redaction am 4. August 1923)

Die bisher über die Zementierungsverhältnisse veröffentlichten Versuche beziehen sich hauptsächlich auf grosse Materialien. So finden wir im Text¹⁾ solch eine Angabe für die Zementierungstiefen wie folgt :—

0.5 mm.	bei 850°	nach 2½ Stunden
1.0 „	„ „	„ 6 „
1.5 „	„ „	„ 8 „

Diese Zahlen kann man doch kaum für die Zementierung kleinen Materials mit z. B. $\frac{1}{4}$ —1 mm. Durchmesser benutzen, weil die Arbeitsverhältnisse bei beiden Fällen nicht gleich sein würden. Die Abhängigkeit des Zementierungsgrades von Temperaturen und von Zeiten muss daher für den Fall der kleinen Materialien aufs neue gemessen werden. Diese Lücke erzielt die vorliegende Arbeit zu erfüllen.

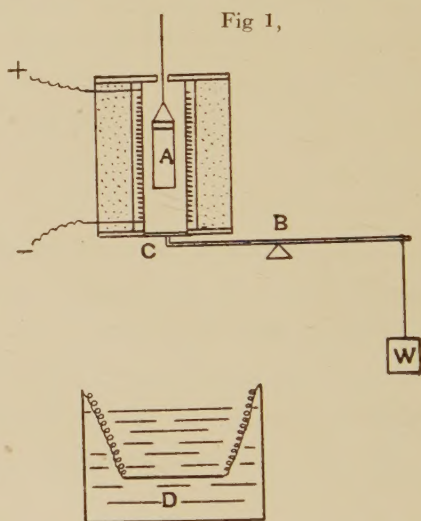
I. ABHÄNGIGKEIT DER ZEMENTIERUNGSGRADE VON TEMPERATUREN UND ERHITZUNGSDAUER.

Auf die Zementierungsgrade üben die Temperaturen und die Erhitzungsdauer einen grossen Einfluss aus.

Ein Bund Eisendrähte von 0.08% C mit einem bestimmten Querschnitte wurde in einem Glaszylinder samt Caron's Zement, welches aus Bariumcarbonat und Kohlenpulver besteht, eingepackt. Fünf solche Zylinder wurden dann in einem elektrischen Ofen bei resp. 800°, 850°, 900°, 950° und 1000° mit verschiedener Zeitdauer erhitzt. Um eine gleichmässige Erhitzung zu ermöglichen, wurden die Temperaturen erst

¹⁾ Guillet, Le Génie Civil, 1911, II, 228.

sehr langsam, ungefähr in 40 Minuten, von 100° bis 800° , und dann sehr schnell bis auf den erwünschten Grad gesteigert. In bezug auf die Zementdichtigkeit, d. h. die Menge des Zements in gr. pro 1000 c.c. der Probe, kann hier darauf aufmerksam gemacht werden, dass für höhere Temperaturen zu grosse Dichtigkeit eher schädlich ist, weil sie, insofern die Masse sehr schnell erhitzt wird, gleichmässige Erhitzung des Bundes verhindert und dadurch unregelmässige Zementierung verursacht. Für die niedrigen Temperaturen, wo das Zement eine sehr geringe Spannung des Kohlenoxyds zeigt, ist grosse Dichtigkeit wünschenswert, insofern die ganze Masse sehr langsam erhitzt wird. Zwar schwankte die Dichtigkeit, die wir gewöhnlich benutzten, zwischen 250—350 gr. pro 1000 c.c. der Probe. Die Einrichtung des Versuchs ist so, wie in Fig. 1 gezeigt. Nach dem rechtzeitigen Erhitzen wurde das Zylinder A durch Öffnen der Unterdecke C mittels eines Hebels B in ein Abschreckungsbad auf dem durch Sprungfeder suspendierten Drahtnetz D gestürzt.



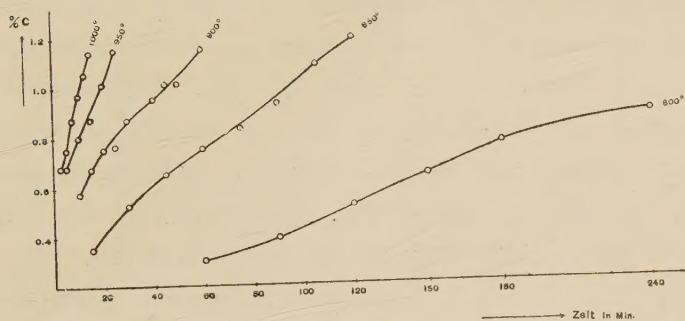
Die zementierten Kohlenstoffmengen, je nach den Temperaturen und Zeiten, sind in der folgenden Tabelle und graphisch in Fig. 2 dargestellt.

TABELLE I.

Versuchs- Nummer	Temperaturen in $^{\circ}\text{C}$	Zeiten in Min.	Zementierter Kohlenstoff in %
1	800	60	0,30
2		90	0,39
3		120	0,52
4		150	0,64
5		180	0,76
6		240	0,86

7	850	15	0.35
8		30	0.52
9		45	0.65
10		60	0.75
11		75	0.83
12		90	0.93
13		105	1.08
14		120	1.19
15	900	10	0.57
16		15	0.67
17		20	0.75
18		25	0.76
19		30	0.87
20		40	0.95
21		45	1.01
22		50	1.01
23		60	1.15
24	950	5	0.68
25		10	0.80
26		15	0.87
27		20	1.01
28		25	1.15
29	1000	2.5	0.68
30		5	0.75
31		7.5	0.87
32		10	0.97
33		12.5	1.05
34		15	1.14

Fig. 2.



II. ABHÄNGIGKEIT DER ZEMENTIERUNGSGRAD E VON DEN GRÖSSEN DER PROBEN BEI VERSCHIEDENEN TEMPERATUREN UND VERSCHIEDENEN ERHITZUNGSDAUER.

Zum Versuche wurden Proben aus derselben Zusammensetzung mit verschiedenem Querschnitte benutzt. Sie sind wie folgt :—

TABELLE II.

Probe- Nummer	Querschnitt in q. mm.	C in %	Mn in %	S in %	P in %	Si in %
1	1.1694	0.08	0.60	0.07	0.015	0.035
2	0.6650					
3	0.4538					
4	0.4073					
5	0.3119					
6	0.2377					
7	0.1886					
8	0.0805					

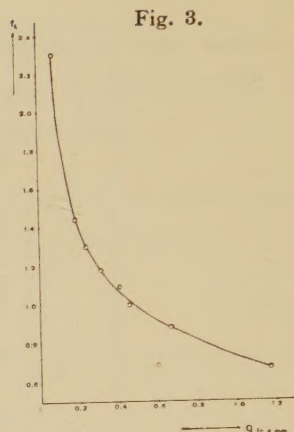
Diese Proben wurden in einige Gruppen geteilt, und jede Gruppe wurde immer mit einigen Stücken der Probe, No. 3, in einem Kasten samt dem Zement eingepackt. Die Zementation geschah für jede Packung bei 800°, 850° und 900° für verschiedene Zeitdauer. Aus den durch Analyse erhaltenen Kohlenstoffmengen für jede Probe wurde ihr ursprünglicher Gehalt an Kohlenstoff abgenommen, und die Reste wurden durch den Wert für die Probe No. 3 die in demselben Kasten eingepackt war, dividiert. Diese Verhältnisse, die wir Zementierungsfähigkeiten, f_z , nennen wollen, sind für jede einzelne Probe von Temperaturen und Zeiten, ebenso wie von der Zusammensetzung²⁾, besonders in bezug auf die ursprünglichen Kohlenstoffgehalte, unabhängig. Sie hängen aber von den Querschnitten in der Weise ab, dass sie mit der Verkleinerung der letzteren zunehmen. Sie werden in der folgenden Tabelle zusammengestellt, und auf Grund derselben ist die Querschnitt-Fähigkeitskurve, Fig. 3, entworfen.

²⁾ Doch bei den mit Kupfer dünn übergezogenen Materialien, obwohl sie vorher mit Schmirkelpapier wohl poliert wurden, waren die Resultate sehr unregelmässig.

TABELLE III.

Probe- num- mer	Zementierungsfähigkeit $\approx f_Q$																	im Mittel
	bei 800°						bei 850°						bei 900°					
	30'	60'	90'	120'	150'	180'	15'	30'	45'	60'	75'	90'	105'	10'	20'	30'	40'	
1			0.65	0.65	0.64	0.65					0.64	0.70	0.67			0.65	0.73	
2			0.89	0.92	0.88				0.79	0.82	0.84	0.96	0.92			0.86	0.95	
3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
4		1.13						1.06	1.04	1.11				1.11	1.10	1.09		
5		1.21	1.25					1.11	1.10					1.18		1.20		
6		1.28	1.33				1.27	1.34										
7	1.56	1.46					1.46	1.48						1.40		1.34		
8	2.54	2.51	2.52				2.61	2.48	2.60	2.00	2.00	1.93		2.56		1.91	2.13	2.23

Mit Hilfe dieser Kurve können wir die Zementierungsfähigkeit einer Probe mit einem beliebigen Querschnitte finden; und wenn wir diese Zahl durch den Kohlengehalt der Probe No. 3, die als Einheit genommen wurde, für irgend eine Temperatur und Zeit multiplizieren, so bekommen wir den Kohlengehalt für die Probe unter den oben genannten Bedingungen.



III. CONSTRUIEREN DES MODELLS HINSICHTLICH DES ZUSAMMENHANGS ZWISCHEN DEN GRÖSSEN, ZEITEN, TEMPERATUREN UND DEM KOHLENSTOFF.

Durch Vereinigung der zwei obigen Resultate kann man ein Modell construieren, das man beim Zementieren benutzt, dass man unter 4 Faktoren, d. h. Querschnitt, Kohlengehalt, Temperatur und Zeiten, wenn beliebige drei bestimmt sind, den anderen errechnen kann.

Bezeichnet man den Kohlenstoffgehalt der Probe No. 3, bei einer Zementierungstemperatur t_1 und Zementierungsdauer z_1 durch $C_{t_1 z_1}^3$ und multipliziert das durch die Zementierungsfähigkeit f_q einer anderen Probe, so bekommt man, wie schon erwähnt, den Kohlenstoffgehalt der letzteren Probe bei t_1 und z_1 . So wurden die Werte, $C_{t_1 z_1}^3 \cdot f_q$, berechnet, und sind in der folgenden Tabelle zusammengestellt:—

TABELLE IV.

Probennummer und Querschnitte in q. mm.	Temperaturen in °C	Zeiten in Minuten	Zementierter Kohlenstoff in %
No. 1, Q=1,1694	800	180	0,51
		240	0,58
	850	75	0,56
		90	0,62
		105	0,72
		120	0,80
	900	30	0,58
		40	0,64
		45	0,67
		50	0,68
		60	0,77
	950	15	0,58
		20	0,68
		25	0,77
	1000	7,5	0,58
		10	0,65
		12,5	0,69
		15	0,76
No. 2, Q=0,6650	800	150	0,56
		180	0,67
		240	0,75
	850	45	0,57
		60	0,66
		75	0,73
		90	0,81
		105	0,95
		120	1,05
	900	15	0,59
		20	0,66
		25	0,67
		30	0,77
		40	0,84
		45	0,88
		50	0,89
		60	1,01
	950	5	0,60
		10	0,70
		15	0,77
		20	0,89
		25	1,01
	1000	2,5	0,60
		5	0,66
		7,5	0,77
		10	0,85
		12,5	0,91
		15	1,00

No. 3, Q=0.4538	800	120	0.52
		150	0.64
		180	0.76
		240	0.86
	850	30	0.52
		45	0.65
		60	0.75
		75	0.83
		90	0.93
		105	1.08
		120	1.19
	900	10	0.57
		15	0.67
		20	0.75
		25	0.76
		30	0.87
		40	0.95
		45	1.01
		50	1.01
		60	1.15
	950	5	0.68
		10	0.86
		15	0.87
		20	1.01
		25	1.15
	1000	2.5	0.68
		5	0.75
		7.5	0.87
		10	0.97
		12.5	1.06
		15	1.14
No. 4, Q=0.4073	800	120	0.57
		150	0.70
		180	0.83
		240	0.93
	850	30	0.57
		45	0.71
		60	0.82
		75	0.90
		90	1.01
		105	1.18
	900	10	0.62
		15	0.73
		20	0.82
		25	0.83
		30	0.95
		40	1.04
		45	1.09
	950	5	0.74
		10	0.87
		15	0.95
		20	1.10
	1000	2.5	0.74
		5	0.81
		7.5	0.95
		10	1.06
		12.5	1.14

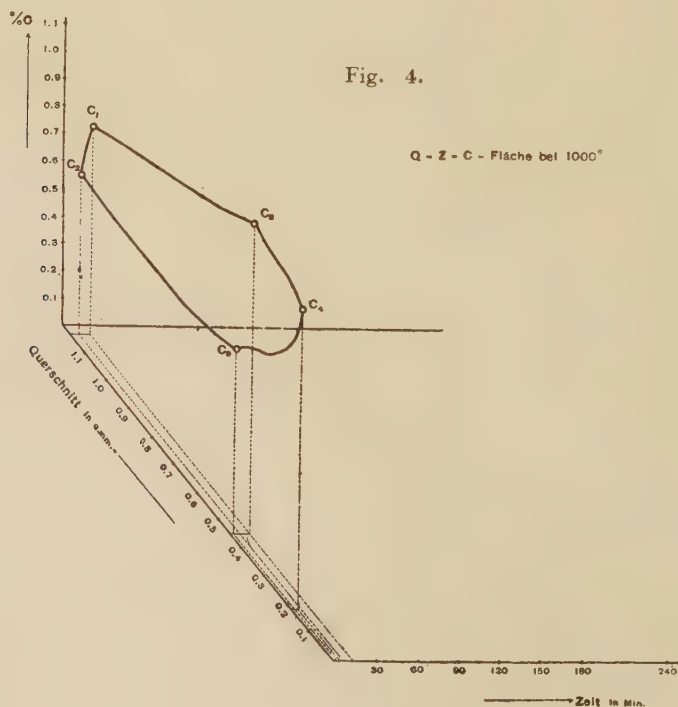
No. 5, Q=0,3119	800	120	0,61
		150	0,76
		180	0,90
		240	1,01
	850	30	0,61
		45	0,77
		60	0,89
		75	0,98
		90	1,09
	900	10	0,67
		15	0,79
		20	0,89
		25	0,90
		30	1,03
		40	1,12
	950	5	0,80
		10	0,94
		15	1,03
		20	1,19
	1000	2,5	0,80
		5	0,88
		7,5	1,03
		10	1,14
No. 6, Q=0,2377	800	90	0,51
		120	0,68
		150	0,83
		180	0,99
		240	1,11
	850	30	0,68
		45	0,85
		60	0,98
		75	1,08
	900	10	0,74
		15	0,87
		20	0,98
		25	0,99
		30	1,13
	950	5	0,88
		10	1,03
		15	1,14
	1000	2,5	0,88
		5	0,97
		7,5	1,13
No. 7, Q=0,1886	800	90	0,56
		120	0,75
		150	0,92
		180	1,09
	850	15	0,51
		30	0,75
		45	0,94
		60	1,08
	900	10	0,82
		15	0,96
		20	1,08
	950	5	0,98
		10	1,15
	1000	2,5	0,98
		5	1,07

No. 8, Q=0.0805	800	60 90 120	0.69 0.90 1.20
	850	15 30	0.81 1.20

Lässt man die Verticalachse Kohlenstoffgehalte C, die Horizontalachse Z, und die Querachse Querschnitte Q representieren, dann entsprechen die Punkte

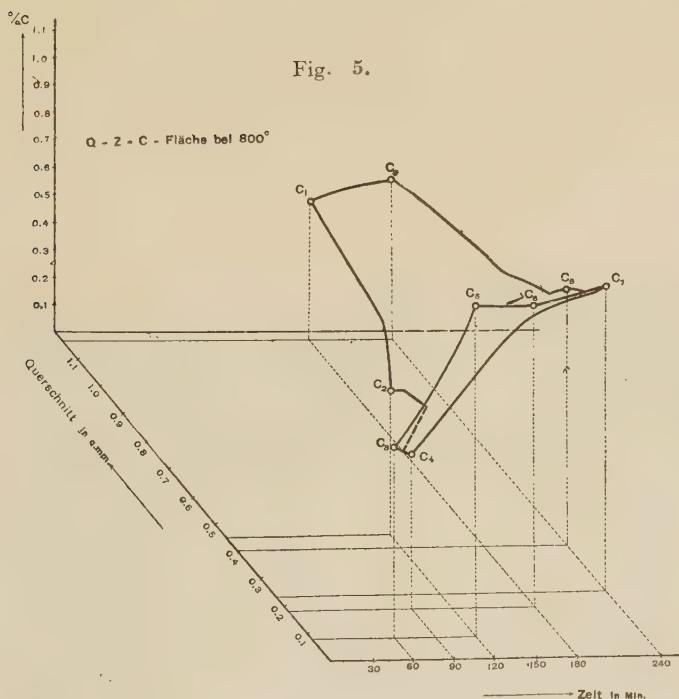
		C	Q	Z	t
C ₁	zu	0.76 %C	1.169 q. mm.	15'	1000°
C ₂	„	0.56	„	7.5	„
C ₃	„	0.63	0.454	2.5	„
C ₄	„	1.04	0.189	5	„
C ₅	„	1.14	0.454	15	„

Das durch diese Punkte begrenzte Gebiet bildet die Q. Z. C—Fläche bei 1000°, wie in Fig. 4 bezeichnet.

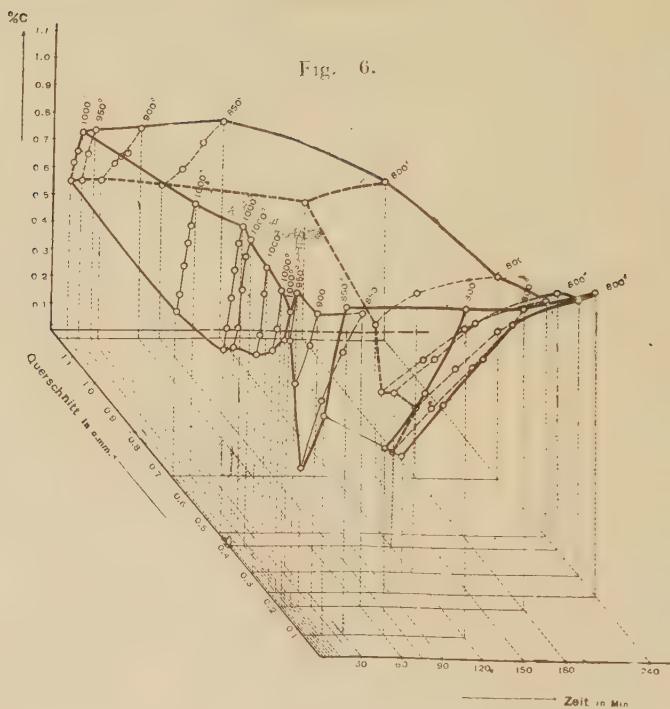


Gleicherweise hat man die Q. Z. C—Fläche für 800°, welche durch die folgenden Punkte definiert und wie Fig. 5 bezeichnet wird:—

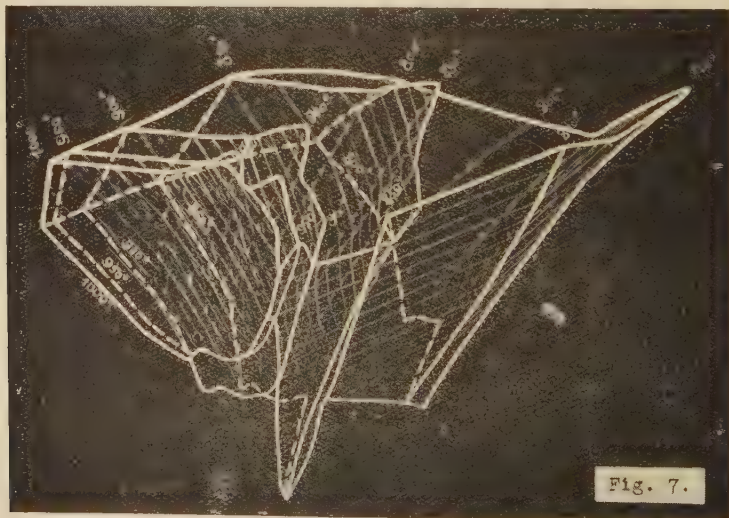
	C	Q	Z	t
C ₁	0.51 %C	1.169 q. mm.	180'	800°
C ₂	0.52	0.454	120	„
C ₃	0.69	0.080	60	„
C ₄	0.56	0.189	90	„
C ₅	1.20	0.080	120	„
C ₆	1.09	0.189	180	„
C ₇	1.11	0.238	240	„
C ₈	0.93	0.407	240	„
C ₉	0.58	1.169	240	„



Wir können noch 3 Flächen für 950°, 900° und 850° gleicherweise herstellen. Durch Kombination dieser 5 Flächen bekommt man ein räumliches Bild wie gezeigt in Fig. 6, wo aber der Einfachheit halber nur 2 Flächen für 1000° und 800° im Voll wiedergegeben sind.



Für das Komplettbild hätte man sich auf das Lichtbild des Modells, Fig. 7, zu beziehen.



Mittels dieses Modells kann man für beliebige Punkte in der Raumfigur ihre Angaben für C, Q, Z, und t interpolieren.

IV. ÜBER DIE ZEMENTE.

Caron's Zemente, von dem wir bei dieser Arbeit mit Vorteil Benutzung machten, besteht, wie wohl bekannt, aus einem Gemische von Bariumcarbonat und Kohlenpulver. Es fragte sich jedoch ob es gleichgültig sei, Calciumcarbonat statt des Bariumsalzes zu gebrauchen. Es ist dies aber nicht der Fall, wie die folgenden Berechnungen zeigen. Über die Wärmedissociation des Calciumcarbonats haben wir unter vielen Autoren Riesenfeldsche Angaben³⁾, die lauten, z. B., 50 mm. P_{CO_2} bei 700°, 99 mm. P_{CO_2} bei 750°, u. s. w. Nun wird CO_2 in Gegenwart von Kohlenstoff in CO reduziert, und beiden Gase kommen bei jeder Temperatur ins Gleichgewicht zu stehen. Für diese Verhältnisse haben wir Boudouardsche Angaben⁴⁾, die lauten, z. B., wie folgt:—

t°	$CO_2 : CO$	P_{CO} in mm.
750	0.24 : 0.76	577.6

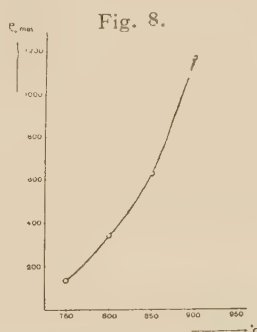
Setzt man nun K_1 =Gleichgewichtsconstant für $CaCO_3$ —Dissociation, und K_2 =dasjenige für CO—Reaktion, so hat man

$$P_{CO} = \sqrt{K_1 \cdot K_2}$$

Nimmt man z. B., $t=750^\circ$ an, so ist $K_1=99$, $K_2=182.9$, und daher $P_{CO}=135$. Gleicherweise berechnet man die Spannungen für die anderen Temperaturen. Die Resultate sind in der folgenden Tabelle zusammengestellt, und auf Grund deren ist die Kurve Fig. 8 entworfen:—

TABELLE V.

t°	P_{CO} in mm.
750	135
800	346
850	636
900	1176

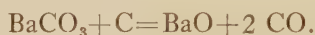


³ J. Chim. Phys. 7, 561 (1909).

⁴ C. r. 130, 132 (1900).

Wie man sieht, ist die Kurve sehr steil, so wie sie schon bei 865° fast 1 Atmosphäre erreicht. Weil die Zementierung aber gewöhnlich bei höheren Temperaturen auszuführen ist, muss die Entstehung des CO demgemäss so rasch sein, dass sie nicht mehr zweckmässig gebraucht werden kann.

Ganz anders ist das der Fall beim Bariumcarbonat. Wie wohl bekannt, ist es in reinem Zustande unter 1.00° schwer zersetzbar; beim Erhitzen zusammen mit Kohlenstoff wird es aber leicht unter 1000° zu zersetzen anfangen. Diese Reaktion wird gewöhnlich, obwohl nicht ganz richtig, mit der folgenden Gleichung ausgedrückt:—



Weil man aber annimmt, dass BaCO_3 sich erst in BaO und CO_2 spaltet, und das letztere dann durch C in CO reduziert wird, so muss die Gasphase auch mit CO_2 , das im Gleichgewicht mit CO steht, vermischt sein. Also muss die Bildung des CO durch die Gleichung



repräsentiert werden. Was die Dissociation des BaCO_3 betrifft, so geht sie nach Finkelstein⁵⁾ in 2 Stufen vor:—



Trotz der geringen Spannung unter 915° muss sie doch noch etwas gelten, weil die Spannung des BaCO_3 durch Beseitigung von CO_2 mittels Kohlenstoffs dann noch leicht erzielen lässt. Da aber die Finkelsteinsche Angabe dafür fehlt, suchte ich die Zahlen von 915° bis nach 750° durch Extrapolieren mit Hilfe der Van t' Hoff'schen Gleichung

$$\frac{d \log_e K}{d T} = - \frac{Q}{R T^2}$$

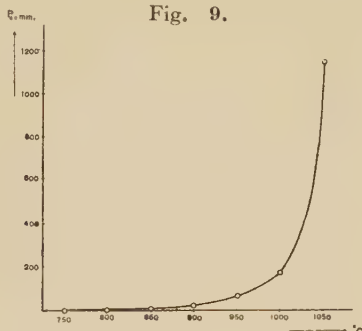
zu ergänzen. Die Resultate sind in der folgenden Tabelle und auch graphisch in Fig. 9 dargestellt:—

⁵ Ber. 39, 1585 (1906).

TABELLE VI.

t°	P_{CO} in mm.
750	0,9
800	3,5
850	9,4
900	23,3
950	65,8
1000	168,6
1050	1149,0

Fig. 9.



Wie aus der Kurve ersichtlich, entwickelt sich die Spannung bei den Temperaturen von 800° bis 1000° , wo der Hauptteil der Zementierung auszuführen ist, ganz regelmässig.

Zusammenfassung :—

1. Abhängigkeit der Zementierungsgrade von Temperaturen und Zeiten für kleine Gegenstände wurde festgestellt.
2. Abhängigkeit der Zementierungsgrade von den Grössen der Probe wurde festgestellt. Daraus wurde die Zementierungsfähigkeit berechnet.
3. Ein Modell, um den Zusammenhang zwischen t° , z , Q und $C\%$ zu zeigen, wurde construiert.
4. Zementierungsvermögen von Calcium- und Bariumcarbonat wurde verglichen.

Herrn Prof. Dr. M. Chikashige spreche ich meinen herzlichen Dank für seine freundliche Unterstützung bei der Ausführung dieser Arbeit aus.

Metallographische Untersuchung über die Nähnadeln

von

Denzo Uno.

(Eingegangen bei der Redaction am 4. August 1923)

Obwohl die Fabrikation der Nähnadeln bei uns schon lange Zeit in Tätigkeit gewesen ist, sind die Erzeugnisse leider doch noch gar nicht tadellos. In einem mit 25 Stück gefüllten Päckchen im Handel sehen wir sehr oft, dass nur einige von guter Beschaffenheit sind, während die anderen entweder spröde sind oder sich biegen oder auch rostig sind.

Entsprechend den Verschiedenheiten der Eigenschaften bemerken wir auch Unterschiede im Feingefüge. Ein vortreffliches Exemplar zeigt eine feine Troosto-martensitische Struktur, wie in Fig. 1, Pl. I. Nicht selten treffen wir aber Exemplare mit Schlackeneinschlusse, wie in Fig. 2, Pl. I, oder mit einem Risse, wie in Fig. 3, Pl. I. Solche Stücke müssen natürliche spröde sein. Auch gibt es wieder andere, die fast nur aus weichem Eisen, wie in Fig. 4, Pl. I, bestehen; diese werden biegsam sein. Zuweilen findet man auch solche mit ungleichmässig zementierter Struktur, wie in Fig. 5, Pl. I; diese werden rostig und spröde sein.

Um die Ursache, woher solch eine Heterogenität der Waren stammt, zu erfahren, werden wir kurz im Folgenden der bei uns herrschende Arbeitsmethode nachspüren.

I. DIE HERRSCHENDE METHODE ZUR HERSTELLUNG DER NÄHNADELN.

Unsere Fabrikanten führen die Zementierung selbst aus, und so sind die Rohmaterialien Eisendrähte mit niedrigen Kohlenstoffgehalte,

wie die folgende Analyse zeigt:—

TABELLE I.

C	Mn	S	P	Si	Cu
0,07—0,08	0,60—0,65	0,05—0,07	0,01—0,02	0,03—0,04	0—0,17

Nach dem Eintauchen in verdünnte Schwefelsäure, um den Rost wegzunehmen, werden die Drähte wassergewaschen und dann mit Kalkwasser gekocht. Nunmehr werden die Drähte durch die Würfel zu einem gewünschten Durchmesser gezogen, zu einer doppelten Nadel-länge geschnitten, nach dem Anlassen gerade gemacht, an den Enden gespitzt, in der Mitte mit zwei neben einander liegenden Löchern versehen, in der Mitte ent zwei geschnitten, und schliesslich jede Hälfte zur Nadelform gebildet. Zwei hundert Stück derselben werden dann aufrecht in einem Tiegel mit Holzkohle zusammen beladen und dann nach mehr-stündigem Ausglühen werden ins Öl abgeschreckt. Sie werden wiederum bei geeigneten Temperaturen angelassen und schliesslich mit einem Gemisch von Öl und Schmirgel zwischen zwei rotierenden Schleifsteinen gut poliert. Sie werden darauf zum Markt in Päckchen, die 25 Stück enthalten, abgeschickt.

Jeder Teil dieser Herstellungsweise muss natürlich unter der wissenschaftlichen Aufsicht geleistet; sonst ist es unvermeidlich, dass die Erzeugnisse nicht immer ganz gleichmässig sein werden. Um die Arbeit gut zu kontrollieren, muss man aber die Arbeitsbedingungen im voraus genau wissen. Bei unseren Fabriken fehlt aber diese Vorsicht.

II. BESCHAFFENHEIT DER GUTEN NÄHNADELN.

Zwecks der Bestimmung der nötigen Beschaffenheit der Näh-nadeln stellten wir zunächst Härte, Tragkraft und Zusammensetzung zusammen mit ihrer Mikrostruktur fest.

Die Messung der Härte wurde durch das Skreloskop Shores vorgenommen. Bei der Messung begegnet man aber grossen Schwierigkeiten wegen der Winzigkeit der Proben, deren Durchmesser nahe der Spitze, wo die Messung stattfinden muss, überhaupt nur unter 0.5 mm. ist. Daher wurde die Messung immer auf derselben Stütze, deren Härte 100 war, mit grosser Vorsicht ausgeführt; trotzdem kann man die Resultate kaum für sehr genau halten.

Zur Bestimmung der Tragkraft musste man bei jeder Nadel in der Mitte den Teil mit fast gleichem Durchmesser abschneiden.

Jedes in der Länge so verkürzte Stück wurde dann an beiden Enden

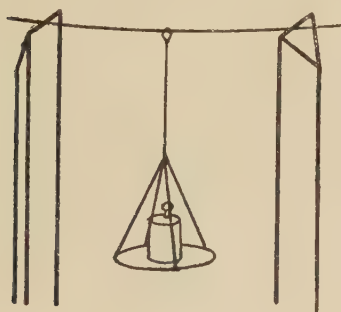


Fig. 1.

gestützt wie in Fig. 1, und durch zunehmendes Gewicht in der Mitte bis zum Brechen gezogen. Die Ablesungen wurden dann auf die Werte bei dem Fall, wo die Stücke mit einem und demselben Durchmesser und der gleichen Länge nur an einem Ende fixiert sind, umgerechnet. Die Resultate sind wie folgt:—

TABELLE. II.

Chem. u. phys. Eigenschaften der guten nicht biegsamen Erzeugnisse.

Exemplar	Zusammensetzung						Härte an der Spitze	Tragkraft Radius=0.38mm. Länge=60mm. in gr.	Mikrostruktur
	C %	Mn %	S %	P %	Si %	Cu %			
I	1.00	0.60	0.07	0.01	0.03	—	70	254	Troost- martensisch
II	0.93	0.60				—	65	178	
III	0.73	0.62				—	62	253	
IV	0.85	0.55				—	65	252	
V	0.89	0.58				—	82	115	
VI	0.75	0.65				0.12	73	198	
VII	0.83	0.70				—	67	125	
VIII	1.10	0.58				0.07	76	125	

Wie aus der Tabelle ersichtlich, ist die Beschaffenheit der guten nicht biegsamen Erzeugnisse ziemlich stark verschieden, so dass der

Kohlenstoffgehalt von 0.73% bis zu 1.1%, die Härte von 62 bis zu 82 und die Tragkraft von 115 gr. bis zu 200 gr. abweicht. So kann man sicher dadurch einen Fortschritt erzielen, dass man die Nähnadeln immer mit einer Härte von über 70 und einer Tragkraft von über 300 gr. (aber nicht biegsam) herstellt. Die beste Zusammensetzung lässt sich dann durch die Erfahrungen gewinnen, wo die obigen Beschränkungen am bequemsten erfüllt werden können.

III. PHYSIKALISCHE EIGENSCHAFTEN DER ZEMENTIERTEN MATERIALIEN NACH KOHLENSTOFFGEHALT, ABSCHRECK- UND ANLASSTEMPERATUREN, EBENSO WIE ABSCHRECKMITTEL.

Die Proben mit 0.7—1.0% C wurden aus Drähten aus weichem Eisen durch Zementierung hergestellt. So bald wie die Eisenstücke zu erwünschtem Kohlenstoffgehalte zementiert waren, wurden sie ins Wasser gestürzt. Die Abschreckwirkung ist dabei nicht stark genug, weil das um die Drähte geklebte Zement ihre gleichmässige Erkaltung verhindert; so wurden die wohl-gewaschenen Abschreckmaterialien unter einer Decke von Holzkohlestückchen schnell wieder bis auf 850° erhitzt und nach dem Erkalten bis auf 780° wieder ins Wasser- oder Ölbad abgeschreckt. Alsdann wurden sie wiederum bis auf 175°, 200°, 225°, 250°, 275°, 300° und 325° resp. zum Anlassen erhitzt.

Die untersuchten Eigenschaften sind Härte, Proportionalitätsgrenze (im Verhältnisse zur Biegungsgrenze stehend), Tragkraft und Brucharbeit.

Über die Härte gilt hier auch, was schon im 2^{ten} Abschnitte gesagt wurde.

Für die Proportionalitätsgrenze und Tragkraft bestimmten wir zuerst die Biegungsgrade der Drahtprobe nach der Belastung und zuletzt die Brucharbeit. An der Belastungs-Biegungskurve sucht man einen Punkt, wo die plötzliche Veränderung der Richtung stattfindet. Der dementsprechende Wert der Belastung wird als Proportionalitätsgrenze angenommen. Den Grenzwert zum Brechen nimmt man dann als Tragkraft an. Zur Messung benutzt man die folgende Einrichtung,

Die Drahtprobe P wird an einem Ende A fixiert. An dem freien Ende C

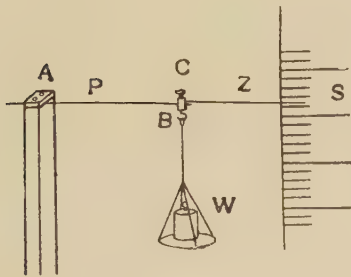


Fig. 2.

werden ein Haken B und ein Draht als Anzeiger Z mittelst einer Klemme befestigt. Durch Anhängen der Belastung W, 10 gr. im Gewicht, wird der Draht sich biegen lassen; die Messung geschieht dann nach einer Minute auf der Skala S mittels des Anzeigers Z. Zur Ablesung benutzt man ein Mikrometermikroskop. Zumehrung der Belastung geschieht mit 10 gr. für jedes Mal.

Für die Bestimmung der Brucharbeit bediente man sich des in Fig. 3 bezeichneten Apparates. An einem langen, mit einem Stativ

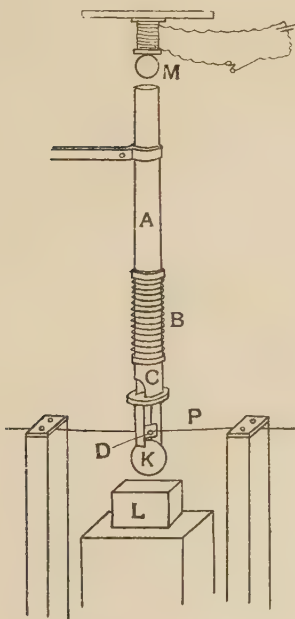


Fig. 3.

senkrecht gehaltenen Glaszylinder A wird der eisernen Zusatz C durch eine Drahtfeder auch senkrecht suspendiert. Als ein Teil dieses Zusatzes besteht D aus einer gehärteten Stahlplatte mit einem Loch, durch welches die an beiden Enden wagerecht befestigte Drahtprobe P im Kontakt mit dem oberen Teil des Loches eingeschaltet wird; K ist eine an den unteren Teil des Zusatzes angelötete Stahlkugel. Die Länge des Zylinders muss so reguliert werden, dass die Arbeit welche durch die fallende Kugel getan wird, nicht zu viel die Stärke der Drähte P übertrifft; auch muss die Lage des Drahtes so berichtigt werden, dass sie gerade in Berührung, aber nicht zur

Stützung des Zylinders steht. Dann kommt noch gerade unter die

Kugel K ein aus einem Gemisch von Öl und Wachs bestehendes weiches Bett L.

Man lässt nun die magnetefasste Stahlkugel M durch Stromaus-schaltung durch das Zylinder auf C fallen. Wenn der Schock nicht genügt, den Draht zu brechen, so wird die Stärke des Drahtes als über dem Produkte vom Gewicht der Kugel $\times$ Höhe registriert. Wenn der Schock gerade die Stärke ausgleicht, so bricht der Draht, ohne die Feder heftig schwingen zu lassen. Wenn aber der Schock grösser als die Stärke ist, dann wird der Rest der Energie das Schwingen der Feder verursachen und demgemäss einen Eindrucke der Kugel K auf dem Bett hervorrufen. Dann misst man die Durchmesser dieser Ein-drücke mit dem Glaslineal Le Chateliers. Andererseits lässt man die Kugel M von verschiedenen Höhen auf C fallen, misst die Durchmesser nach den Höhen und bekommt es eine Arbeits-Durchmesserkurve. Vermöge dieser Kurve kann man die dem Durchmesser entsprechenden Arbeitsmengen erfahren, welche man aus dem Arbeitstotal subtrahiert; der Rest ist ohne weiteres die Stärke des Drahtes. Fig. 4 zeigt uns klar diese Beziehung.

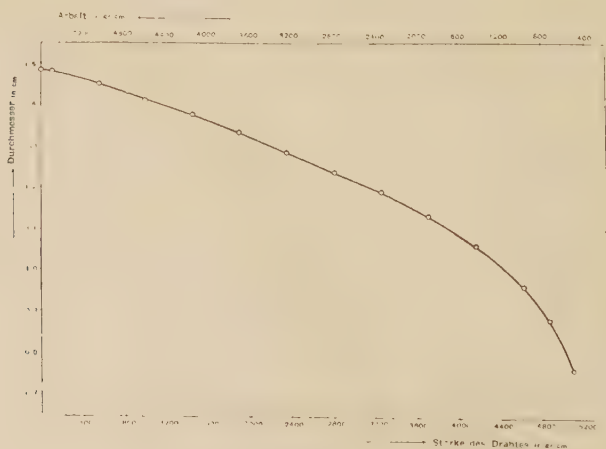


Fig. 4.

Die Messungen zusammen mit den Beschreibungen der Probe sind in der folgenden Tabelle zusammengestellt:—

TABELLE III.

Kohlenstoff in %	Abschreckmittel	Anlasstemp. in °C	Zeichen	Härtezahl	Tragkraft in gr.	Proportionalitätsgrenze in gr.	Brucharbeit in gr. cm.
0.7	Öl	175	a ₁	69	270	—	750
		225	a ₃	66	310	—	1550
		250	a ₄	64	430	300	2600
		275	a ₅	49	—	260	—
	Wasser	225	a ₃	64	280	—	950
		250	a ₄	70	350	—	2120
		275	a ₅	56	—	280	2900
		300	a ₆	50	—	220	—
0.8	Öl	225	b ₃	69	280	—	1320
		250	b ₄	74	350	—	2120
		275	b ₅	56	—	280	2600
	Wasser	250	b ₄	78	320	—	1700
		275	b ₅	65	410	320	2250
		300	b ₆	54	—	240	3000
0.9	Öl	225	c ₃	75	270	—	1370
		250	c ₄	78	340	—	2140
		275	c ₅	64	—	270	2500
	Wasser	250	c ₄	79	310	—	1620
		275	c ₅	71	480	—	2080
		300	c ₆	61	—	260	2600
1.0	Öl	225	d ₃	77	240	—	980
		250	d ₄	80	330	—	1750
		275	d ₅	65	380	290	2380
	Wasser	250	d ₄	82	290	—	1520
		275	d ₅	71	380	—	1890
		300	d ₆	66	500	280	2350
		325	d ₇	60	—	210	—

Um diese Resultate graphisch darzustellen, legt man ein grosses Viereck mit einem Diagonal senkrecht in der Mitte des Papiers an und teilt je zwei parallele Seiten resp. in 7 Teile für t° und 4 für Kohlenstoff. In ihm werden dann die Punkte, welche a_n, b_n, c_n und d_n entsprechen, gekennzeichnet. Durch jeden dieser Punkte zieht man nun je eine senkrechte und horizontale Linie, auf deren vier Enden die physikalischen Angaben resp. nach den Abscissi mit Kreisen für Wasser- und mit Vierecken für Ölhärtung gekennzeichnet werden. Verbindet man die Kreise oder Vierecke je für die Proben mit denselben Zusammensetzungen, so bekommt man 4 Eigenschaftslinien

für jede wasser- und ölabgeschreckte Probe. Verbindet man dagegen die Kreise oder Vierecke durch dieselben Anlasstemperaturen, so bekommt man auch 7 Eigenschaftslinien (mit gebrochenen Linien bezeichnet) nach den Temperaturen. Vergl. Fig. 5 und 6.



Fig. 5.

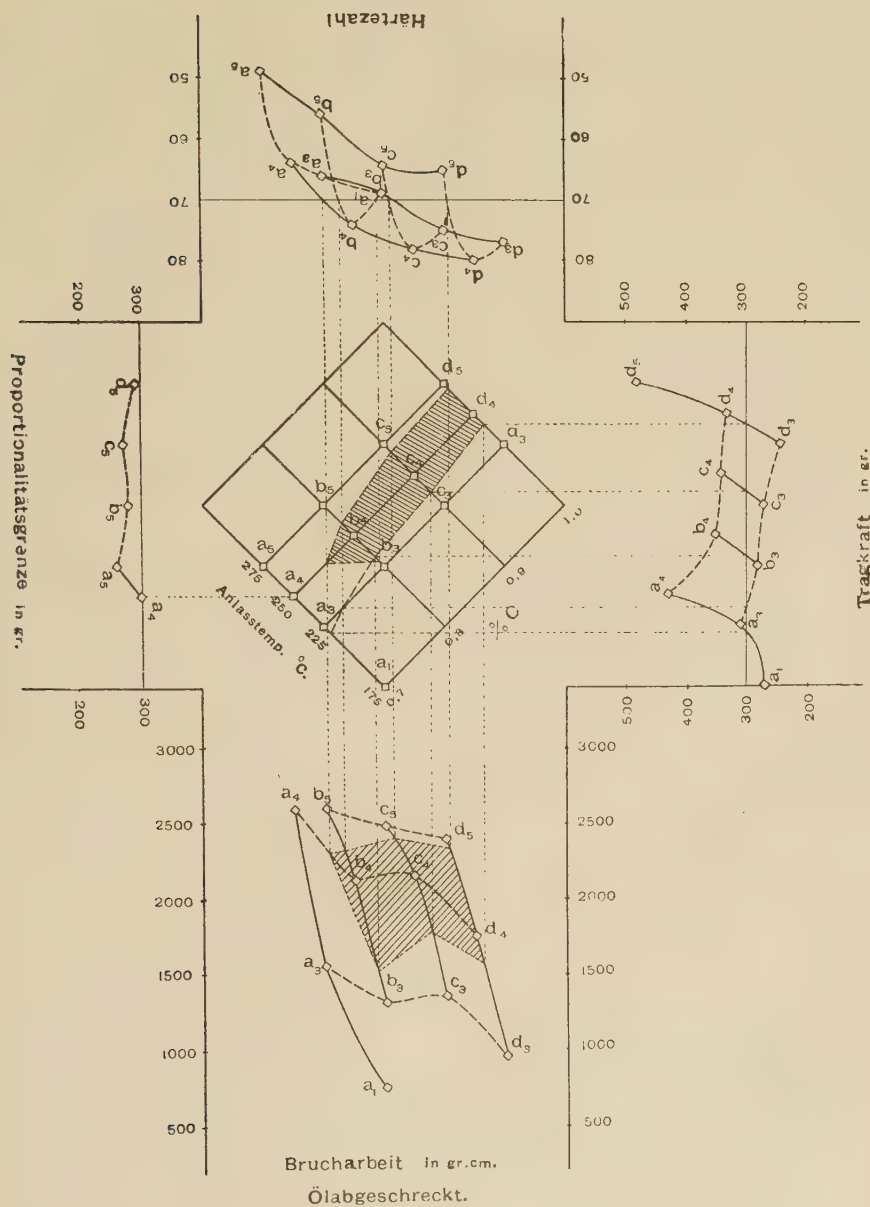


Fig. 6.

Um die Proben mit Härte über 70 und mit Tragkraft und Proportionalitätsgrenze, beide über 300 gr., zu finden, zieht man je eine gerade Linie bei 70 und 300 durch die entsprechenden Abscissen, welche die Voll- und gebrochenen Linien in mehreren Punkten schneiden. Die Lagen dieser Schnittpunkte werden nun wieder im Mittelviereck zurückgetragen. Die Linien, welche die Punkte derselben Art je mit einander verbinden, begrenzen die schraffierten Felder mit den erwünschten Eigenschaften.

Wenn man nun noch die Beschränkung für Brucharbeit dazu fügen will, so lässt man die Grenze der schraffierten Felder in dem Brucharbeitsgebiet übertragen und merkt die Umfänge auf, wo die gesuchten Eigenschaften erfüllt werden. Diese Umfänge werden wiederum im Mittelviereck zurückgetragen. Alle Punkte im entsprechenden Gebiete müssen alle Bedingungen, wie im Anfang erwünscht, erfüllen.

Aus der Übersicht dieser schraffierten Felder kann man ersehen, dass die besten Nadelproben ihre Beschränkungen zwischen 240° bis 270° für Anlasstemperaturen und 0.75% bis 1.0% C haben. Da aber die Arbeitssicherheit in Betracht genommen werden muss, könnte man sicher einen Kohlenstoffgehalt von 0.9% und eine Anlasstemperatur von 250° bei der Ölhärtung und 265° bei der Wasserhärtung als am geeignetsten annehmen. Dabei kann man natürlich die Drähte der perlitischen Zusammensetzung im Handel benutzen; nicht mehr notwendig ist es dann, die Zementierung selbst zu schaffen.

IV. ERFOLGE.

Die auf Grund dieser Beschränkungen hergestellten Nadeln waren immer sehr hart und stark, und auch nicht biegsam und zeigten die feine Troosto-martensitische Struktur, wie in Fig. 6, Pl. I, gezeigt.

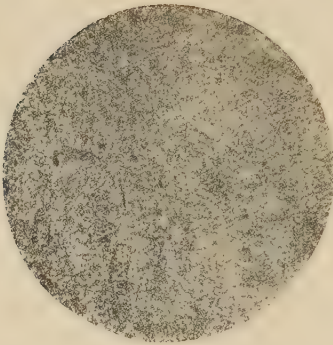
ZUSAMMENFASSUNG.

1. Die für Nähnadeln nötige Beschaffenheit wurde gefunden.
2. Ein Apparat zur Messung der Brucharbeit wurde entworfen.

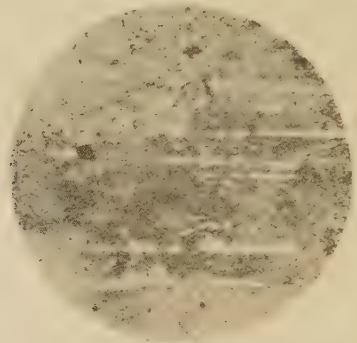
3. Die Bedingungen für die Herstellung der Proben mit der nötigen Beschaffenheit wurden festgestellt.

Zum Schluss sage ich Herrn Prof. Dr. Chikashige für seine freundliche Hilfe bei der Ausführung dieser Arbeit meinen besten Dank aus.

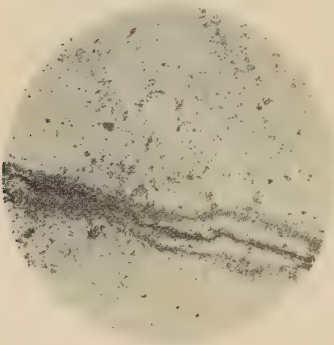
Pl. I.



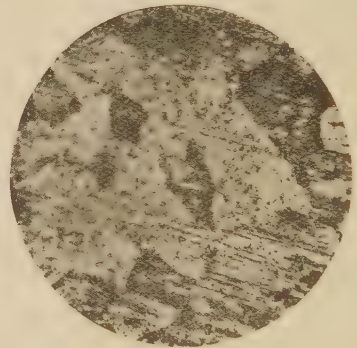
Troost-martensit, 100 f. Verg.
Fig. 1.



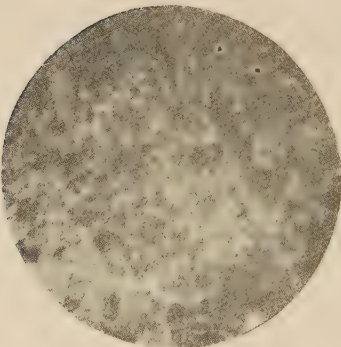
Schlackeneinschluss, 100 f. Verg.
Fig. 2.



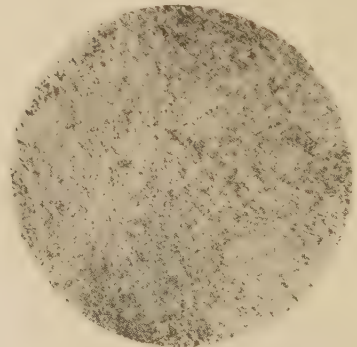
Riss, 100 f. Verg.
Fig. 3.



Nicht zementiertes weiches Eisen,
400 f. Verg.
Fig. 4.



Ungleichmässige Zementierung
300 f. Verg.
Fig. 5.



Troost-martensit, 100 f. Verg.
Fig. 6.

Studies on Catalytic Action, V.

Catalytic Reduction of α and β -Naphthyl Methyl Ethers.

By

Shigeru Komatsu and Shinichiro Kumamoto.

(Received Sept. 21, 1923).

In the first communication on the subject¹, a brief account was given on the investigation of the catalytic reduction of α -naphthol and α -naphthylamine, yielding 10% ar-compounds and 90% ac-compounds in the former, and 90% ar-compounds and 10% ac-compounds in the latter respectively. The cause of the difference in the yield of the ar- and ac-compounds in both α -derivatives of naphthalene, which was explained by regarding α -naphthol as a condensed compound of phenol and benzylalcohol, and α -naphthylamine analogously as a united one of aniline and benzylamine. It may also be attributed to the difference of the electronic nature of the groups substituting H _{α} atom of the naphthalene molecule; the NH₂ group having a strong basic character compared with the OH group, exerted a certain amount of influence on the naphthalene molecule to prevent the hydrogenation of the substituted nucleus, accordingly in α -naphthylamine the ar-compounds predominate in the reduced compounds compared with the case of naphthol as shown in the experiment.

When α -naphthol was transformed into the methyl ether, the basic character of the oxygen atom in the compound by replacing the hydrogen atom combined with the oxygen atom with the methyl group²

¹ These Memoirs. **6**, 177 (1923).

² A. Wurtz : Atomic theory, 7th Ed., 250 ; J. H. van Hoff : Ansichten ü. Org. Chem., **63**. (1877), N. Collie and Tickle : J. Chem. Soc., **75**, 710 (1897), A. Baeyer und Villiger : Ber. D. Chem. Ges., **34**, 2679, 3612 (1901); **35**, 120 (1902); J. Schmidt : u. d. Basischen Eigenschaft. d. Sauerstoffs u. Kohlenstoffs, 1904.

was evidently strengthened and consequently the OCH_3 group should naturally be expected to exert an influence similar to that observed on the NH_2 group in naphthylamine, on the hydrogenation of the naphthyl ether, with a greater yield of ar-compounds than the ac-one.

NH_3	OH_2
base	neutral.
$\text{N}(\text{CH}_3)_3$	$\text{O}(\text{CH}_3)_2$
strong base	weak base.

α -Naphthyl methyl ether¹ used in this experiment, was prepared by the interaction of 270 grm. α -naphthol purified by steam distillation, and 450 grm. dimethyl sulphate in 500 c.c. 15% caustic soda solution at ordinary temperature, the reaction product alkalined with 600 c.c. 30% caustic soda solution, was then subjected to steam distillation to isolate the ether, and the oily layer in the distillate, separated from the aqueous part, was purified by distillation after drying with sodium sulphate and then with fused caustic soda. It boiled at $67-9^\circ$, and the yield was 229 grm. which corresponds to 77% of the theory.

175 grm. of the ether were passed with the purified hydrogen gas on the reduced nickel heated at 200° , and 150 grm. of the reaction product obtained.

It was subjected to the fractional distillation under ordinary pressure as usual for about 20 times, and was separated into the following ten portions :

Fractions.	Yield.	
	in grm.	in mol.
1. $204-206^\circ$	0.8	0.006
2. $210-214^\circ$	3.5	0.030
3. $216-220^\circ$	1.0	0.008
4. $230-240^\circ$	1.6	0.012
5. $240-243^\circ$	2.7	0.016
6. $245-250^\circ$	4.2	0.044
7. $250-253^\circ$	7.0	0.088
8. $254-258^\circ$	14.0	0.099
9. $258-260^\circ$	15.8	
10. above 260°	58.1	
	108.7	

¹ V. Meyer and P. Jacobson : *Lehrbuch d. Organ. Chem.*, II, 2, 365.

The chemical analysis and the determination of the physical constants were made of each fraction and the results were as follows :

1. The fraction, B. p. 204–206°, Tetrahydronaphthalene¹.

It was found to consist of tetrahydronaphthalene¹, by analysis and determination of density and the index of refraction.

C=90.55 ; H=8.93 (theory requires C=90.84 ; H=9.16 for C₁₀H₁₂) and $n_D^{25^*}=1.5494$; $d_4^{25^*}=0.9767$.

2. The fraction, B. p. 210–214°, Dihydronaphthalene.

The results of the analysis, C=92.49 ; H=8.93, and the determination of the physical constants, $n_D^{25}=1.5499$; $d_4^{25}=0.9878$, agree fairly well with those of dihydronaphthalene obtained by other chemists².

3. The fraction, B. p. 216–220°, Naphthalene.

Expecting that the fraction consisted of naphthalene and some other hydrocarbons, it was treated with the alcoholic solution of picric acid to isolate naphthalene, whereas yellow needle crystals separated, which, after being purified by recrystallisation, were confirmed to be naphthalene picrate by determination of melting point³(149°).

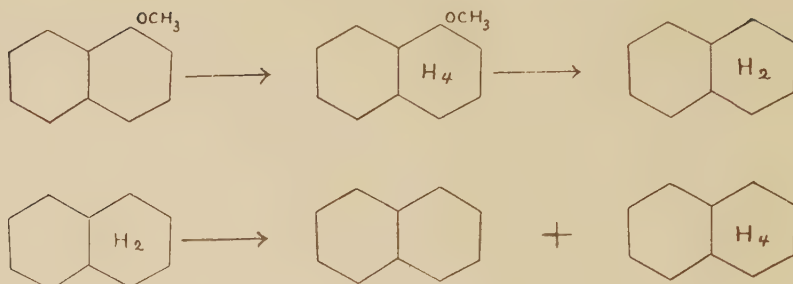
The formation of naphthalene and its hydrogenated hydrocarbons in the course of the catalytic reduction of the ether, was explained by assuming the formation of dihydronaphthalene by the decomposition of ac-tetrahydronaphthyl methyl ether which was regarded to be formed simultaneously with ar-tetrahydronaphthyl ether by the catalytic reduction of the naphthyl ether ; dihydronaphthalene partially transformed catalytically into naphthalene and tetrahydronaphthalene, as H. Wieland⁴ has already observed on dihydronaphthalene, which by shaking with palladium black dissolved in benzene, yields naphthalene and tetrahydronaphthalene, and the remainder evidently reduced by the catalytic action of hydrogen and nickel to tetrahydronaphthalene :

¹ Beilsteins Handbuch d. Org. Chem., 4 Auf., V, 491 (1922).

² Ibid., 518.

³ V. Meyer and P. Jacobson : Lehrbuch d. Organ. Chem., II, 2, 323.

⁴ Ber. D. Chem. Ges., **45**, 486 (1912) ; and also refer A. Mailhe and M. Murat : Bull. soc. chim., (4), **11**, 122 (1912).



4. The fraction, B. p. 229—231°,

The analytical results indicate that the fraction consists of a mixture of hydrocarbon and ether : C=87.07 ; H=8.45.

5. The fraction, B. p. 245—248°, α -ar-Tetrahydronaphthyl Methyl Ether.

Its theoretical value for the elementary composition and methoxyl value agrees with the experimental results of the fraction : C=80.93 ; H=8.70 ; OCH_3 =18.28. $n_D^{25}=1.5700$; $d_4^{25}=1.0413$.

6. α -ar-Dihydronaphthyl Methyl Ether. (Δ^6 and Δ^7).

The analytical results and methoxyl determination indicate the fractions B. p. 254—256° and B. p. 250—252°, consist of pure α -ar-dihydronaphthyl ether though the methoxyl value of the fractions showed a slight difference compared with the theoretical one for the ether.

The fraction, B. P. 250—252° : C=82.51 ; H=7.83 :

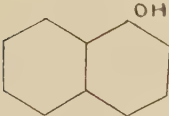
The fraction, B. p. 254—256° : C=82.38 ; H=7.74 ;

OCH_3 =18.33, $d_4^{25}=1.5768$; $n_D^{25}=1.5768$; theory requires C=82.50 ; H=7.50 ; OCH_3 =19.38. for $\text{C}_{10}\text{H}_9\text{OCH}_3$.

Two structural formulae (Δ^6 and Δ^7) for α -ar-dihydronaphthyl ether are theoretically possible but their decision was remained.

When α -naphthyl methyl ether was reduced catalytically with hydrogen and nickel at a temperature of 200°, it yielded 19% α -compounds and 81% ar-compounds calculated on the molecular weight basis, and thus our expectation was realised.

The authors¹ attention was directed to the examination of the relative yield of ac- and ar-compounds in the reduction of the naphthols and the results compiled from many experiments were summarised in the following table :

	Temp.	Ac-comp. %	Ar-comp. %
	{ 150 ^{o1}	85	15
	{ 135 ²	89	11
	{ 110 ²	56	44
	{ 135 ⁴	—	100
	{ 150 ^{o1}	75	25
	{ 135 ³	60	40
	{ 135 ⁴	79	21

When we examine the above figures in detail, the following conclusions were drawn : 1. the rate of formation of the ac-compounds increase with rise of temperature, 2. the velocity of the formation of ac-compounds in the case of β -naphthol is much more retarded than in α -isomer, so that under the same experimental conditions, it yielded 75% ac-compounds in the former but 85% in the latter. The second conclusion may be explained, if we adopt the hypothesis of steric hindrance ; the spatial disposition of the OH group to the non-substituted nucleus— the neighbouring benzene nucleus of the naphthalenemolecule, effects the chemical character of the molecule as a whole, in the catalytic reduction of the naphthols, to result as described above in details.

The catalytic reduction of β -naphthyl methyl ether was undertaken to study whether a steric hindrance which could be encountered in the reduction of the ethers, resembled that observed in naphthols.

The sample used in the experiment was obtained from the

¹ A. Brchet and R. Cornubert : Bull. soc. chim., (4), **31**, 1280 (1922).

² S. Komatsu and R. Nodzu : These Memoirs, **6**, 177 (1923).

³ S. Komatsu and I. Nishimatsu : Unpublished work.

⁴ E. Bamberger & W. Lodter : Ber. D. Chem. Ges., **23**, 197 (1890) ; E. Bamberger & M. Kitschelt : Ibid., **23** 885 (1890) ; E. Bamberger and F. Lengfeld : Ibid., **23**, 1124 (1890)

market and was purified by steam distillation in an alkaline solution, and distillate collected, and this was found to melt at 72°.

155 grm. of the sample were reduced catalytically with reduced nickel at 200° and the product amounting to 123 grm., after repeated distillation under ordinary pressure for about 20 times, was separated into the following 7 portions :

Fractions.	Yield.	
	in grm.	in mol.
1. 203—205°	20	0.152
2. 211—213°	1	0.008
3. 215—225°	22	0.008
4. 238—250°	3	0.020
5. 252—255°	40	0.244
6. 256—258°	3	0.020
7. above 258°	13	
	81	

The results of the analysis and of the determination of the physical constants of each fraction, were as follows :

1. The fraction, B. p. 203—205°, Tetrahydronaphthalene.

It gave on analysis C=91.07; H=8.50, (theory requires C=90.84; H=9.16 for $C_{10}H_{12}$), $n_D^{25^\circ}=1.5490$; $d_4^{25^\circ}=0.984$.

2. The fraction, B. p. 211—213°, Dihydronaphthalene.

It gave on analysis C=91.62; H=8.08 (theory requires C=92.31; H=7.69 for $C_{10}H_{10}$).

3. The fraction, B. p. 215—225°, Naphthalene.

It was supposed that this portion consisted partly of naphthalene which was confirmed by transforming it into picrate as usual.

4. The fraction, B. p. 238—250°, β -ar-Hexahydronaphthyl Methyl Ether.

The analytical results of this fraction giving C=80.84; 81.02; H=8.38; 8.34, agree fairly well with those of hexahydronaphthyl methyl ether which require C=80.49; H=9.76, however, confirmation was lacking due to the small quantity.

5. The fraction, B. p. 252—255°, β -ar-Tetrahydronaphthyl Methyl Ether.

It gave on analysis C=81.38; H=8.49; $CH_3O=18.45$, a

result which agrees with the theoretical values $C=81.48$; $H=8.64$; $CH_3O=19.14$ for tetrahydronaphthyl methyl ether, and also gave the physical constants $n_D^{25} = 1.5437$; $d_4^{25} = 1.0344$.

6. The fraction, B. p. 256--258°, β -ar-Dihydronaphthyl Methyl Ether.

It gave on analysis $C=82.13$; $H=7.97$; $CH_3O=18.80$, and the constants $n_D^{25} = 1.5800$; $d_4^{25} = 1.0605$, the theory requiring $C=82.50$; $H=7.50$; $CH_3O=19.38$ for $C_{10}H_9OCH_3$.

Of the reaction products from β -naphthyl ether, by the catalytic reduction at 200°, we obtained 37% ac-compounds and 63% ar-compounds, and the former calculated from the yield of the hydrocarbons, since they were regarded as formed from the ac-hydronaphthyl ether by catalytic action of reduced nickel at high temperature and ordinary pressure, as explained in the case of α -isomer.

It is the intention of one of the authors (S. Komatsu) of this paper to discuss in the next article how finely divided reduced nickel acts to promote dehydration, under certain condition, as reduced copper does¹.

It was noteworthy fact that α -naphthyl methyl ether by reduction with metallic sodium and boiling amyl alcohol, instead of hydrogen and finely divided nickel yields only ar-tetrahydronaphthyl methyl ether, B. p. 245—248°, given on analysis $C=80.72$; $H=8.83$.

β -Isomer, analogously, was resulted by the same treatment to form ar-tetrahydronaphthyl methyl ether, $C=81.31$; $H=8.28$. When, however, β -ether reduced with metallic sodium and ethyl alcohol, it yields a new hydrogenated ether boiled at 256—258°, which was confirmed to be β -ar-dihydronaphthyl methyl ether by analysis $C=82.49$; $H=7.44$.

As a matter of fact, the atomic groups possessing a basic character such as NH_2 or OCH_3 , when combined with α or β carbon atom of the naphthalene molecule, facilitate the formation of ar-compounds in the catalytic reduction of naphthalene derivatives, while

¹ S. Komatsu: These Memoirs, 7. 85 (1923).

the methoxyl group replaced by the hydroxyl group of non-basic nature in the naphthalene molecule, retards their formation. We, however, must confess that we are still ignorant of the reasons why the atomic group of basic character retards the formation of ac-compounds, and why the spatial disposition of the methoxyl group in naphthalene, exerts an influence on the formation of ac-compounds— the only term, so far as we know, to call such phenomena is “steric hindrance”.

July, 1923. Laboratory of Organic and Bio-chemistry.

On the Composition of Japanese Petroleum, II.

By

Shigeru Komatsu and Naozo Tanaka.

(Received Sept. 21, 1923)

In the first article, one of us and S. Kusumoto¹ made a communication on the isolation of cyclohexane and methylcyclopentane from the Nishiyama oil, Echigo. The present study is concerned with the identification of benzene and n-hexane isolated from the oil, which were regarded as having the most intimate relation to these naphthenes described in the previous article with respect to the genetic formation from the vegetable or animal kingdom.

The presence of benzene in the Nishiyama oil is undoubted since it has been proved that the main part of the fraction B. p. 70—90°, constitutes of cyclohexane which can be transformed catalytically into benzene and vice versa.

Moreover, S. Takano has reported that the fraction B. p. 80—82°, of the Amaze oil, Echigo, yielded by nitration 22% of dinitrobenzene², and the results of other investigators³ show that petroleum from many parts of the world contained benzene to some extent.

¹ These Memoirs, **7**, 77 (1923).

² Engler- Höfer : Das Erdöl, I, 360 ; There arises a question with the formation of the nitro compound, since naphthenes by treating with concentrated nitric acid yield some nitro aromatic compounds, (S. K) and also refer Balbiano : Chem. Z. 1902, II, 402 ; W. Markownikoff : Ber. D. Chem. Ges., **33**, 1908 (1900) ; Lieb. Ann., **307**, 342 (1899).

³ Engler- Höfer : Das Erdöl, I, 361.

BENZENE.

The fraction B. p. 70—90°, of the Nishiyama oil was treated with fuming sulphuric acid containing 7% SO_3 , and the acidic solution separated from the oil part, was diluted with ice, neutralized with calcium hydroxide, filtered off calcium sulphate, and an excess of lime in the solution was removed by means of carbon dioxide, the filtrate free from the carbonate was treated with sodium carbonate to convert calcium benzene sulphonate formed in the solution by above treatments into the sodium salt, and then the solution was evaporated to dryness. It gave 12 gramm. of the sodium salt which was subjected to the alkali fusion with 21 gramm. caustic soda, and the oily substance generated by the fusion, amounting to 2.2 gramm., was fractionated twice under ordinary pressure after drying with anhydrous sodium sulphate.

1st. fraction	below 182°	0.6 gramm.
2nd. „	182—183°	0.8 „

The second fraction solidified in fine needle crystals, and shows the violet colour reaction with ferric chloride solution and the Liebermann reaction for the nitroso compounds. It was analysed and the results $\text{C}=73.55$; $\text{H}=6.45$, being small compared with the calculated value for phenol $\text{C}=76.55$; $\text{H}=6.43$, show that some aliphatic alcohols might be present as an impurity.

It was then treated with benzoyl chloride in the alkaline solution to get phenol in a pure state, according to the direction of Baumann¹, and also of Behal and Choay,² and the benzoic acid ester thus formed after purification as usual, was found to melt at 69—69.5°.

It gave on analysis the following results $\text{C}=78.95$; $\text{H}=5.22$, which agree well with the theory $\text{C}=78.8$; $\text{H}=5.1$ required for $\text{C}_{13}\text{H}_{10}\text{O}_2$.

¹ Ber. D. Chem. Ges., **19**, 3218 (1886).

² C. R. **118**, 1211 (1894).

By the treatment with fuming sulphuric acid, the benzene in the oil yields benzene sulphonic acid which, by alkali fusion and benzylation, is transformed into phenol, and then into phenol denzoate successively. It was thus proved by chemical means that benzene is present in the Nishiyama oil.

NOR. HEXANE.

To isolate the hydrocarbon, the fraction B. p. 40—75°, $d_4^{25^\circ} = 0.697$ of the Nishiyama oil was carefully fractionated under ordinary pressure seven times in a dephlegmator with two columns, and the fraction B. p. 66.5—71°, $d_4^{25^\circ} = 0.6938$ weighing 94 grm. was subjected to oxidation with con. nitric acid (1.5), following the directions of S. Young¹. Cyclopentane, its methyl derivatives, and isohexane, these isomeric substances of n-hexane were oxidized by this treatment, whereby n-hexane remains partly unaffected by the action of con. nitric acid. The reaction product washed with water and dilute alkali solution and dried with calcium chloride, and then it was subjected to fractional distillation on metallic sodium four times under ordinary pressure.

	Fraction.	Yield.	
1.	below 68.5°	1.9 grm.	
2.	68.5—69.5°	1.6 „	$d_4^{25^\circ} = 0.6708$
3.	69.5—70.5°	1.5 „	

To get n-hexane in a pure state, the fractionation was continued, and after the 7th. distillation under 749 m.m., the fraction B. p. 67.5—68° 5' was analysed C=83.05 ; H=15.93, $d_4^{25^\circ} = 0.66863$.

¹ J. Chem. Soc., **73**, 906 (1898).

The other fractions B. p. 66.5—67.5° and B. p. 68.5—69.5° were combined together, and the mixture fractionated nine times under ordinary pressure, and the fraction B. p. 71—73° was analysed with the following results :

$$C=83.80 ; H=15.80 ; d_4^{20} = 0.67178.$$

Thus, we may conclude that the Nishiyama oil surely contains n-hexane though the analytical figures and the density of the fraction B. p. 67.5—68.5 under 749 m.m. show a slight difference compared with the calculated percentage for n-hexane, and the density observed by other chemists of the hydrocarbon isolated from petroleum¹ and of the synthetic one².

July 1923. Laboratory of Organic and Bio-chemistry.

¹ Engler and Höfer : *Das Erdöl*, I. 244 ; Brooks : *The non-benzenoid hydrocarbons*. p. 99, 548.

² Beilstein : *Handbuch d. Org. Chem.*, 4 auf. I, 143 (1918).

On Beckmann's Rearrangement, X.

By

Shigeru Komatsu

(Received Oct. 29, 1923)

A few words concerning the continuation of this research in the author's laboratory seem called for here. In 1907, Professor M. Kuhara communicated the first paper on this subject to the *Memoirs of Science and Engineering of the University*. Subsequently, until 1918, nine papers were issued in co-operation with fellow-investigators, but the problem has not yet been satisfactorily solved.

In 1919, the Chair of Organic Chemistry was kindly bestowed on the author, one of Prof. Kuhara's old students, and the research on the subject came to be undertaken here again, since it would have grieved the author greatly to give up the greatest work of his life which was being carried on right up to the very day of his death. Besides, it is also the sincere desire of the author's colleagues to follow in the steps of their grand father in chemistry. The hypothesis, however, on which further work in this field is based may not be in every respect the same as the teacher's.

-
- ¹ M. Kuhara & T. Kainosho : On Beckmann's Rearrangement I, *Memoirs of Coll. Science & Eng.*, **I**, 254 (1907); M. Kuhara & Y. Toda : II, *Ibid.*, **II**, 387 (1910); M. Kuhara & T. Okada : III, *These Memoirs*, **1**, 1 (1914); M. Kuhara & K. Suitsu : VI, *Ibid.*, **1**, 25 (1914); M. Kuhara, K. Matsunomiya & N. Matsunami : V, *Ibid.*, **1**, 105 (1914); M. Kuhara & H. Watanabe : VI, *Ibid.*, **1**, 349 (1916); M. Kuhara & F. Ishikawa : VII, *Ibid.*, 355 (1916); M. Kuhara, N. Agatsuma & K. Araki : VIII, *Ibid.*, **3**, 1 (1917); M. Kuhara & K. Kashima : IX, *Ibid.*, **4**, 69 (1920).

The intramolecular conversion of an oxime into its isomeric acid amide, the so-called Beckmann rearrangement, can usually be effected by the mineral and organic acids, acid anhydrides and acid chlorides. Their employment as reagents, however, is likely to bring about misapprehension that the *raison d'être* of the rearrangement, as the author had conjectured, was due to the effect of the dehydration of the oxime, on account of these numerous reagents which are commonly used as the dehydrating agent in organic chemistry. Such unwarranted assumption of the cause of the change will be proved to be erroneous by mentioning here a few interesting examples of the Beckmann change noticed by O. Baudisch¹ in the transformation of acetone oxime into methyl acetamide by the action of the ultraviolet ray, and also by the author's co-operators on the catalytic action of reduced copper on various oximes².

The reaction for the nitrile formation from oxime by action of these reagents, which actually taking place by the removal of water from the oxime, was sometimes confused with the Beckmann reaction. The mechanism for the formation of benzonitrile from anti-benzaldoxime will be a different from that for the acetonitrile formation from diacetyl monoximine benzoylester³.

The nitrile formation, in general, from the oxime should be explained in two different manners: one is the direct formation and the other is the indirect. The formation of *o*-cyano diphenyl carboxylic acid from α -nitroso- β -naphthol⁴, benzonitrile from the oximes of benzoyl formic acids⁴, camphonitrile from camphor oxime⁵ and menthonitrile from menthone oxime⁶ should be classified as belonging to the indirect formation. In the latter case which was formerly named 'Beckmannsche

¹ Ber. D. Chem. Ges., **44**, 1009 (1911); A. Werner: Lehr. d. Stereochem., 278 (1904).

² These Memoirs, **6**, 245 (1923); **7**, 151 (1923).

³ O. Diels and M. Stern: Ber. D. Chem. Ges., **40**, 1630 (1907).

⁴ A. Werner and A. Piguet: Ibid., **37**, 4310 (1904).

⁵ These Memoirs, **6**, 245 (1923).

⁶ Ibid., **7**, 151 (1923).

Umlagerung zweiter Art¹ by A. Werner, two entirely different reactions occur successively: the rearrangement of oxime into acid amide or isoxime (in cyclic compound) and the dehydration of the acid amide by the action of the same reagent used for bringing the rearrangement, which immediately followed the molecular conversion. The examples which afford supply the supposition for the author's interpretation for the indirect nitrile formation, can easily be cited here from literature, and they are: the reaction between phosphorus pentachloride and pivalophenone oxime² or benzoyl piperidine³ and that between phosphorus pentaoxide and menthone oxime⁴.

The conversion of cinnamyl aldoxime into isoquinoline has been misunderstood by chemists as an abnormal manifestation of the Beckmann change⁵ which was also considered by the author to be very nearly true in explaining that the cinnamyl formamide yielded by the Beckmann change from the oxime, suffers dehydration as a result of forming isoquinoline as final product. V. Meyer and P. Jacobson⁶ have distinguished the nitrile decomposition from the Beckmann change in the case of the menthone oxime. They made no distinction between the nitrile decomposition and 'Beckmannsche Umlagerung zweiter Art.' The differences between these reactions, however, are principally due to differences in the mechanism of these reactions as already stated above.

The Beckmann reaction is the hitherto employed unique method for determining the configuration of an oxime from its products of transformation since adopted by Hantsch to distinguish the isomeric oximes⁷. There were, however, very curious examples of the Beckmann change

¹ A. Werner and A. Piguet: Loc. cit.; O. Diels: Lieb. Ann., **432**, 1 (1923).

² G. Schroeter: Ber. D. Chem. Ges., **44**, 1204 (1911).

³ J. v. Braun: Ibid., **37**, 2915 (1904).

⁴ O. Wallach and F. E. Tuttle: Lieb. Ann., **277**, 157 (1893).

⁵ J. B. Cohen: Org. chem. for advan. stud., 1907, 213.

⁶ Lehr. d. Org. Chem., II, **1**, 897 (1902); also refer A. Kötze and Wunsdorf: J. prac. Chem., **88**, 519 (1913); O. Wallach: Lieb. Ann., **329**, 105 (1903).

⁷ Ber. D. Chem. Ges., **24**, 22 (1891).

observed by E. Beckmann and Köster¹, and other chemists², which resulted in the same ultimate reaction products though they started in the reaction with isomeric oximes.

Consequently the author was inclined to side with the opinion of S. Schroeter³ and others that the reaction is not a reliable method for distinguishing stereoisomerides of oximes unless the great care is taken in the conversion of oximes by the action of heat and light, and also by some treatments into one another.

Oct. 1923. Laboratory of Organic-and Bio-Chemistry.

¹ Lieb. Ann., **274**, 15 (1893).

² S. Schroeter : Ber. D. Chem. Ges., **44**, 1204 (1911) ; A. Werner & A. Piguet : Loc. cit ; J. Meisenheimer : Ber. D. Chem. Ges., **54**, 3206 (1921) ; S. Yamaguchi : Unpublished work.

³ Loc. cit, and also refer to Annual reports of the progress of chemistry XIX, 95 (1923).

Catalytic Action of Reduced Copper on laevo-Menthone Oxime.

(On Beckmann's Rearrangement, XI)

By

Shigeru Komatsu and Masao Kurata.

(Received Oct. 29, 1923)

One of the present authors and S. Yamaguchi¹ have reported that when dextro-camphor oxime passed with pure hydrogen on reduced copper heated at 200°, it yielded α -campholenamide, α -campholenic acid and α -camphenitrile, and that these compounds were assumed to be derived from camphorisoixime, a hypothetical substance, by the catalytic action of the reduced copper, which resulted from the Beckmann rearrangement of the camphor oxime. The isolation of the isoxime from the reaction product did not succeed, due to its unstable nature *vis-à-vis* chemical reagents or heat, being spontaneously transformed into the compounds mentioned above.

The menthone oxime, however, is interesting on account of the fact that it undergoes the Beckmann rearrangement by being treated with conc. sulphuric acid to give stable menthonisoxime² which corresponds to camphorisoixime in constitution and other respects, and the isoxime by dehydration yields menthonitrile³. The present experiment, therefore, was undertaken with the expectation of isolation menthonisoxime, and thereby to bring strong support for the present authors'

¹ These Memoirs, **6**, 245 (1923)

² Lieb. Ann., **277**, 156 (1893); **278**, 304 (1894); **329**, 105 (1903).

³ Lieb. Ann., **278**, 309 (1894).

opinion that the rearrangement of the oxime would be effected by the catalytic action of the reduced copper.

laevo-Menthone was prepared from 90 gm. menthol, following Beckmann's directions¹, and 78 gm. of the pure ketone B. p. 205—206°, $d_4^{25}=0.8903$, $[\alpha]_D^{25}=-28.3^\circ$, were obtained. It was transformed into its ketone oxime as usual, which showed $[\alpha]_D^{25}=-44.0^\circ$ in an alcohol solution, and the yield was 91% of the theory.

40 gm. of the oxime were passed in an interval of 16 hours, with pure hydrogen on reduced copper heated at 200°, which was prepared from 9 gm. of copper oxide, and repeating the operation five times, 167 gm. of the reaction product of a light reddish-coloured liquid were obtained. In the course of the reaction, a deposit of white crystals was noticed at the end of the reaction tube, and also the evolution of ammonia gas, the former melting at 103—106° and greatly resembling decylenic amide² in property.

The product separated from the bluish water layer which formed during the reaction, was treated with aqueous ammonia, dilute hydrochloric acid and water successively to separate the acidic, basic, and neutral substances from each other, and the each portion was subjected to the following treatment :

I. ACIDIC SUBSTANCE

Decylenic Acid.²

A substance was, on acidifying the ammonia extract with dilute sulphuric acid, separated out from the solution, which on being extracted with ether, dried with anhydrous sodium sulphate, and dry ammonia gas passed in, gave an insoluble ammonium salt.

It yields silver salt with silver nitrate, and was assumed to be decylenic acid, but was not further examined, owing to lack of material.

¹ Lieb. Ann., **250**, 325 (1889).

² Ibid., **296**, 126 (1897).

II. BASIC SUBSTANCES.

1. *laevo*-Menthyl Amine.¹

The acidic extract, on alkalifying with caustic solution, yields oily basic substances which separated from the solution, suspended in water and passed in carbon dioxide gas, separate into two parts; one is soluble in the carbonic acid solution and the other is insoluble.

The free bases isolated from the carbonic acid solution, boiled at 203—218°, amounting to 1.1 gm., and yielded the acetates and the oxalates with the following melting point :

	M. p. of the salts of the bases	M. p. of salts of the	
		mixture of the bases and 1-menthyl amine	mixture of the bases and menthonyl amine
Acetate	151—152°	127°	—
Oxalate	158°	163—164°	142—143°

The melting point determination of the salts indicate that the sample was a mixture of two or more bases.

The hydrochlorides of bases, therefore, were treated with absolute ether to separate 1-menthyl amine salt from the other substance, the insoluble salt (m. p. above 260°) with platinum chloride gave yellow crystals of the double salt which melt at 203—204°, and gave on analysis the following results :

Pt=25.50, theory requires Pt=25.80 for $(C_{10}H_{12}NHCl)_2PtCl_4 \cdot 2H_2O$.

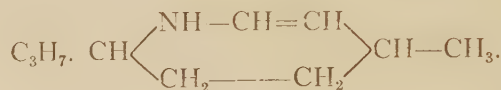
Its properties and analytical results agree well with those of 1-menthyl amine platinum chloride prepared from menthone oxime by reduction.

The other hydrochloride which was soluble in the ether solution, melted at 190—220°, being quite different in its properties from menthonyl amine salt, was regarded as consisting of d-menthyl amine salt and an other salt. Further examination of this part, however, was not carried out.

¹ A. Mailhe and M. Murat : Bull. soc. chim., (4), 9, 464 (1911).

The insoluble bases in carbonic acid solution.

2. γ -Methyl- α' -isopropyl cyclohexene-imine,



The basic substances were fractionated into two portions ;

1. B. p. 235—300°, yield 3.4 grm. pale yellow oil.

2. B. p. 300—320°, 3.6 yellow oil.

The first fraction was subjected to steam distillation, and the oily substance distilled with steam, extracted with ether, transformed into the hydrochloride and then into a double salt of chloroplatinate, which shrinks at 187° and melts at 206° with decomposition after purification and was analysed with the following results :

C=32.75 ; H=4.92 ; Pt=26.48, theory requires

C=33.52 ; H=5.63 ; Pt=27.25 for $\text{C}_{20}\text{H}_{40}\text{N}_2\text{PtCl}_6$.

It resembles piperidine of its odour, and seems to be an unsaturated base by its chemical properties, and was considered as formed by the catalytic dehydration of reduced copper on γ -methyl- α' -isopropyl cyclohexanolimine¹ which resulted from menthonisoxime by reduction.

3. Dimenthyl amine.²

The second fraction, B. p. 300-320°, was treated with hydrochloric acid to convert the amine which was regarded as forming the main part of the fraction into the hydrochloride, the salt was transformed into the double salt of platinum chloride which melts at 196° with decomposition.

For confirmation, it was analysed with the following results :

C=46.11 ; H=7.83 ; Pt=19.85 (theory requires C=48.17,

H=8.09 ; Pt=19.58 for $(\text{C}_{20}\text{H}_{40}\text{NCl})_2 \text{PtCl}_4$).

III. NEUTRAL SUBSTANCES.

¹ O. Wallach : Lieb. Ann., 324, 301 (1902).

² Bull. soc. chim., (4), 9, 464 (1911).

This portion was subjected to steam distillation to separate the volatile part from the nonvolatile, and the former was subjected to fractional distillation :

	Fraction	Yield	Nitrogen	
1.	205—210°	111.4 gm.	—	colourless
2.	210—250°	7.8	+	light yellow
3.	above 250°	2	+	brownish yellow
		121.2		

1. Menthone.

The first fraction was confirmed to be a mixture of isomenthone and 1-menthone by the determination of the physical constants of the purified sample, B. p. 205—206°, by distillation : $d_4^{25}=0.8912$; $[\alpha]_D^{25}=-4.0^\circ$.

2. Menthonitrile.

The second fraction was reduced with metallic sodium and alcohol, and the reaction product was separated into two parts, one was neutral and the other basic, and the former amounting to 6.6 gm. was confirmed to be menthol by its properties, and the latter amounting to 0.34 gm. was also identified to be 1-menthonyl amine¹ by transformation into the oxalate.

M. p. 162°; N=5.83 (by Duma's method), theory requires N=5.51 for $C_{10}H_{21}NC_2H_5O_4 \cdot \frac{1}{2}H_2O$.

The isolation of the amine from the neutral reaction product by reduction, supports the theory of the existence of menthonitrile in it. The detection and the isolation of menthonisoxime of the reaction products were attempted but ended in negative results.

Of 84 gm. reaction product from 100 gm. 1-menthone oxime, 60 gm. menthone, 2 gm. dimethylamine, 1 gm. 1-menthyl amine with some d-menthyl amine, 0.2 menthonitrile, a small quantity of decylenic acid and its amide, and γ -methyl- α' -isopropyl cyclohexene-imine were isolated and confirmed.

Of these substances, 1-menthone, 1-menthyl amine and dimethyl

² Lieb. Ann., 278, 314 (1891).

amine were reported as having been obtained by A. Milhe and M. Murat¹ from 1-menthone oxime by catalytic reduction with hydrogen and nickel.

It may, therefore, be concluded that the catalytic action of reduced copper on menthone oxime resembles in some respect, that of the reduced nickel, and on the other hand, the formation of menthonitrile and decylenic acid resembles that of concentrated sulphuric acid and phosphor pentoxide.

Menthonitrile and decylenic acid were supposed to be derived by catalytic dehydration and hydration of decylenic amide respectively, this last mentioned amide being regarded as an intermediate compound in the transformation of menthonisoxime into the nitrile and the acid.

Although the authors could not succeed in the isolation of menthonisoxime, its momentary formation, in the course of the reaction, will be admitted by the isolation of the compound supposed to be γ -methyl- α' -isopropyl cyclohexene-imine, and accordingly we can no more deny that 1-menthone oxime suffers the Beckmann rearrangement, by the catalytic action of reduced copper.

The catalytic action of reduced copper on the oxime, which has been described above, is not only a new example of the Beckmann change but is of interest for the sake of the fact that it accelerates both reactions, hydration and dehydration of the acid amide, and the latter reactions will be discussed fully in another paper.

Sept. 1923. Laboratory of Organic and Bio-chemistry.

¹ Loc. cit.

Studies on Catalytic Action, VI.

Catalytic Action of Reduced Copper on Acid Amide.

By

Shigeru Komatsu and Masao Kurata.

(Received Oct. 29, 1923)

One of the authors (S. K.) has claimed that reduced copper acts on alcohols as a catalyst of dehydration at high temperature¹. The authors have observed that the molecular conversion of menthone oxime by the catalytic action of reduced copper into menthonisoxime was accompanied by the simultaneous formation of menthonitrile and decylenic acid². To confirm the latter fact, two compounds were derived from menthonisoxime by catalytic dehydration and hydration or hydrolysis of reduced copper, menthonisoxime prepared from menthone oxime by the action of conc. sulphuric acid, was passed on reduced copper heated at 200°, and the formation of menthonitrile and decylenic acid as the authors had expected, were observed, the former was confirmed by its smell and other chemical properties, and the latter by transforming into its silver salt.

This fact leads the authors to the notion that these opposed reactions—the hydration and dehydration—of the acid amides, actually take place simultaneously the catalytic action of reduced copper at high temperature. The formation of campholenic acid and campholenitrile from camphor oxime³, and of benzonitrile from acetophenone oxime⁴,

¹ These Memoirs, 7, (1923).

² Ibid., 7, (1923).

³ Ibid., 6, 245 (1923).

⁴ S. Yamaguchi: unpublished work.

were cited here as examples to support our assumption. Such assumption seems to us highly probable since the catalyst, in general, is capable, under different conditions, of exercising a catalytic influence in promoting the opposite reaction.

To make sure whether or nor this anticipation was accurate, 7.6 grm. benzamide M. p. 127—128°, were passed on reduced copper heated at 250°, during an interval of three hours. The products escaped from the reaction tube, condensed in the first receiver cooled with ice water, and the escaped ammonia gas was absorbed in the second one which was filled with dilute hydrochloric acid. On opening the apparatus, the characteristic smell of benzonitril was noticeable.

The reaction product in the first receiver, amounting to 7.4 grm., was treated with dry ether, the insoluble acid amide filtered (amounting to 6.2 grm.), and passed in dry ammonia gas to precipitate benzoic acid as the ammonium salt and filtered. The yield of ammonium benzoate was 0.7 grm. 0.5 grm. of benzoic acid were obtained in pure state from the salt.

It melts at 121°, and gave on analysis the following results ;

C=68.48 ; H=5.13, theory requires C=68.85 ;

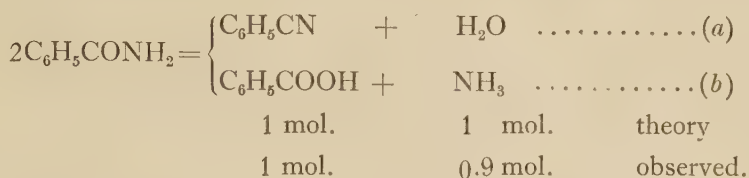
H=4.92 for $C_7H_5O_2$.

On distilling off the solvent of the ethereal solution separated from the ammonium salt, there remains an oily substance possessing the odour of benzonitrile, which was reduced metallic sodium in alcoholic solution to an amine. The amine isolated from the reaction products was converted into the hydrochloride which amounted to 0.2 grm., then converted into the double salt with platinum chloride, and analysed with the following results :

Pt=31.64, theory requires Pt=31.28 for $C_{12}H_{16}N_2PtCl_6$.

The quantity of ammonia in the second receiver, which was generated from the acid amide by reaction, was found to be 0.074 grm., by titration, which showed agreement with the required value 0.086 grm., calculated from the quantity of ammonium benzoate.

The chemical reactions which occurred by the interaction between the acid amide and the reduced copper at 250°, will be involved in the following equations :



When benzamide comes into contact with reduced copper at 250°, as stated above, dehydration (a) will take place, decomposing it into benzonitrile and water, and the water generated by the reaction acts on the amide immediately, in presence of the catalyst, to hydrolyse it into benzoic acid and ammonia (b); namely, benzamide by the contact action of the reduced copper suffers simultaneously dehydration and hydration.

Acetamide, analogously, behaves toward the catalyst; a pure sample when passed on the reduced copper heated at 200°, was decomposed into acetic acid, ammonia and acetonitrile. Acetic acid and ammonia were identified by the usual chemical methods, and the nitrile was recognized by its characteristic smell and also by reducing it to methyl amine.

The authors, therefore, venture to affirm that reduced copper under certain conditions, promotes simultaneously both reactions, dehydration and hydration, or hydrolysis of the monobasic acid amides.

It will be noticed that our reaction compared with the Cannizzaro reaction shows the parallelism existing between the two reactions.

Sept. 1923. Laboratory of Organic-and Bio-Chemistry.

A New Method for the Isolation of Sucrose from the Mixture of Glucose, Fructose and Sucrose.

By

Shigeru Komatsu and Minoru Tanimura.

(Received Oct. 27, 1923)

The processes for the isolation of pure d-glucose and d-fructose by fractional crystallisation in the glacial acetic acid solution of their mixture with or without sucrose, were described in the study of the kaki-fruit¹. The preparation of pure crystalline sucrose from such a mixture was a tedious task especially when it was found in smallest proportions compared with other sugars, notwithstanding that sucrose crystallizes from the concentrated solution with remarkable facility.

The principle from which the new method was derived, was to isolate the sucrose after separating the reducing sugars from the solution by oxidation, transforming them into insoluble salts of the sugar acids.

To attain this purpose, the oxidation of sugars in a neutral solution is preferable, since the reducing sugars, by this treatment, were all converted into sugar acids, while the sucrose remains in the solution, being unaffected by the action of the oxidizing agent.

The method for oxidizing the sugars with bromine water in presence of calcium carbonate has been investigated. The necessity of precipitating and removing the calcium gluconate and other calcium salts formed by the reaction, from the solution makes the method inconvenient.

The oxidation with the yellow oxide of mercury instead of bromine water, in presence of calcium carbonate, will be appreciated

¹ S. Komatsu and H. Ueda: *J. Biochem.*, **1**, 181 (1922); S. Komatsu and M. Ishimasa: *Ibid.*, **2**, 301 (1923).

equally with the bromine method in yielding gluconic acid and other sugar acids from glucose and fructose, and also in leaving sucrose in the solution, unaffected by the action of the reagent¹. Moreover, the employment of yellow mercuric oxide as an oxidizing agent obviates the trouble of removing calcium bromide from the solution, and consequently facilitates the isolation of sucrose found in any proportion in the sample.

A solution was made of 4 gm. sucrose and 6 gm. d-glucose in 100 c.c. of water. This mixture was then treated according to the directions suggested by A. Blanchetière² with 25 gm. yellow mercuric oxide and 10 gm. calcium carbonate. After boiling for 2 hours, the solution was filtered from the mercurous oxide and mercury formed, concentrated to small volume under reduced pressure, and the calcium salts of the acids formed by the oxidation of the reducing sugars were precipitated by the addition of alcohol. In order to precipitate completely the calcium salts only, the percentage of alcohol in the solution should be kept at 80% by volume in the solution while sucrose remains; of the sugars remaining in the solution, 36% was glucose and 64% sucrose, calculated by the reducing power of Fehling's solution before and after inversion.

A solution of 4 gm. sucrose, 3 gm. d-glucose and 3 gm. d-fructose in 100 c.c. of water, was oxidized with 25 gm. mercuric oxide and 10 gm. calcium carbonate, in the same manner as before.

The solution separated from mercury, mercurous oxide and calcium salts of organic acids, which was ascertained to contain 1.8 gm. of the reducing sugar and 2.9 gm. sucrose, (ratio 1:1.6) was concentrated under reduced pressure to a thick syrup. The syrup was poured out of the flask and mixed thoroughly with 2 volumes of hot glacial acetic acid. After cooling to room temperature, it was seeded with sucrose and set aside to crystallize in an ice-cooled chamber. The sucrose

¹ O. v. Lippmann: D. Chem. Zuckerarten (1904), 1229, 1277.

² Bull. soc. chim., (4), 33, 345 (1923).

A New Method for the Isolation of Sucrose from a Mixture of Glucose, etc. 163

crystallized in white lumps was separated from the mother liquor and washed with alcohol and ether and then dried as usual. The yield was 1.1 gm. which corresponds to about 40% of theory.

The sample recrystallized from the ethyl alcohol solution, melts at 181°, and showed the following constant-specific rotation in a 1dm. tube :

$$[\alpha]_D^{21} = \frac{22.42 \times 10}{0.3351} = +66°.68$$

SUMMARY

Sucrose was isolated in crystalline state from the mixture of glucose, fructose and sucrose, after transforming the reducing sugars into the sugar acids by the oxidation of yellow oxide of mercury in presence of calcium carbonate.

It was found necessary to keep the solution in neutral to reduce the hydrolysis of sucrose.

The sucrose was crystallized from the glacial acetic acid solution as usual.

Oct. 1923. Laboratory of Organic and Bio-Chemistry.

On the Biochemical Study of the Ripening of the Kaki-fruit, VI.*

Isolation of Sucrose from the Kaki-fruit.

By

Shigeru Komatsu and Motaro Ishimasa.

(Received Oct. 27, 1923).

It was reported¹ that sucrose was found with d-glucose and d-fructose in the fruit, by means of inversion with dilute acids, and also that² the quantity of sucrose in the fruit changing along with the fruit life, was in inverse proportion to that of the reducing sugars.

As to the season for attaining the maximum quantity of sucrose in the fruit, according to the authors' observation it seems to be just before the maturity of the fruit, no matter what variety and where it was grown; namely in Kyoto, it was the end of September with the sweet variety, and the beginning of October with the astringent one.

Consequently, care should be taken in choosing the season most suitable for the isolation of sucrose from the fruit.

The sample used in the present experiment was "Gosho-Kaki", the sweet variety grown in Tanaka, Kyoto, was secured through the courtesy of Mr. Uno.

It was picked on Oct. 4th, and was a light orange yellow in colour, with a slightly astringent taste.

* The expenses of this investigation were shared by the Department of Education.

¹ J. Biochem., **1**, 193 (1922); **2**, 308 (1923).

² Ibid.,

30 fruits weighed 2233 grm. (74 grm. per fruit), and the pulp was prepared as usual, weighing 2080 grm. and this was boiled with 4500 cc. water for one hour to extract the sugars. 4800 c.c. of the extract were treated with basic lead acetate to separate the pectin and shibuol from the solution, and filtered, passed in sulphurated hydrogen gas, and then filtered. The clear filtrate amounting to 4450 c.c., showed $[\alpha]_D = +0.45^\circ$ in dm. tube, and contained 71 grm. d-glucose, 56 grm. d-fructose and 53 grm. sucrose which calculated by means of the reducing power of the Fehling solution and angle of rotation, before and after inversion, and these amounts correspond to 6.2% reducing sugars 2.6% sucrose in pulp.

To isolate sucrose only, the filtrate was concentrated to 630 c.c. under reduced pressure, 100 c.c. of the solution (11 grm. d-glucose 9 grm. d-fructose and 8.5 grm. sucrose) were oxidized according to the method proposed by one of us and M. Tanimura, with 75 grm. mercuric oxide and 30 grm. calcium carbonate whereby the reducing sugars were all oxidized into sugar acids, sucrose only remaining in the solution unaffected by the action of the oxidizing agent.

The reaction was completed in two hours, and the insoluble salts filtered off, and the filtrate showed no reducing action toward the Fehling solution, was concentrated into a small volume under reduced pressure, poured into 150 c.c. 94% alcohol to thrown down the calcium salts of the sugar acids, and filtered. The filtrate was concentrated again and treated with alcohol, and the operation repeated three times. The final solution containing 2.2 grm. sucrose calculated by means of the reducing power of the Fehling solution after inversion, was concentrated to syrup under reduced pressure.

Pure sucrose was obtained in a crystalline state from the syrup as usual, using glacial acetic acid as solvent, and amounted to 1.4 grm. (70% of the theory). The purified sample from ethyl alcohol solution melts at $182-183^\circ$, and showed the optical rotatory power,

¹ E. O. von Lippmann; *Die Chem. d. Zuckerarten*, IIte. Auf. 1066 (1904).

$$\left[\alpha \right]_D = \frac{100 \times 1.070}{1.607} = +66.60 \text{ in 1 dm. tube.}$$

It showed no mutarotation, and was hydrolysed by acids and also by the invertase into the reducing sugars, and gave on analysis the following results :

C=41.8 ; H=6.6 ; theory requires C=42.1 ; H=6.4 for $C_{12}H_{22}O_{11}$

The second crop crystallized from the mother liquor separated from the first crop, was 0.6 gm. and melted at 178—179°.

It was, thus, confirmed that sucrose actually exists in the Kaki-fruit.

In conclusion, the authors wish to express their indebtedness to Mr. Uno, for the donation of the material for this research.

Oct. 1923. Laboratory of Organic-and Bio-Chemistry.

Vol. VII, No. 3, Published March 10th, 1924

Price - - - Yen 1.00

These Memoirs are on sale at

MARUZEN COMPANY, LTD.

TOKYO, OSAKA, KYOTO, NAGOYA, YOKOHAMA, FUKUOKA
& SENDAI.

大正十三年三月五日印刷

大正十三年三月十日發行

編纂兼發行者 京都帝國大學理學部

印刷者 飯田彌之助

大阪市西區土佐堀通四丁目八番地

印刷所 株式會社 三有社

大阪市西區土佐堀通四丁目八番地

賣捌所 丸善株式會社

東京、大阪、京都、名古屋、橫濱、福岡、仙臺

CONTENTS.

Über die Zementierung Kleiner Eisenstücke. Von Denzo Uno.	107
Metallographische Untersuchung über die Nähnadeln. Von Denzo Uno.	135
Studies on Catalytic Action, V. Catalytic Reduction of α and β -Naphthyl Methyl Ethers. By Shigeru Komatsu and Shinichiro Kumamoto. . . .	135
On the Composition of Japanese Petroleum, II. By Shigeru Komatsu and Naozo Tanaka.	143
On Beckmann's Rearrangement, X. By Shigeru Komatsu.	147
Catalytic Action of Reduced Copper on laevo-Menthone (On Beckmann's Rearrangement, XI) By Shigeru Komatsu and Masao Kurata.	151
Studies on Catalytic Action, VI. Catalytic Action of Reduced Copper on Acid Amide. By Shigeru Komatsu and Masao Kurata	157
A New Method for the Isolation of Sucrose from the Mixture of Glucose, Fructose and Sucrose. By Shigeru Komatsu and Minoru Tanimura.	161
On the Biochemical Study of the Ripening of the Kaki-fruit, VI. Isolation of Sucrose from the Kaki-fruit. By Shigeru Komatsu and Motaro Ishimasa.	165
